

Description

CERAMIC MULTI-LAYER COMPONENT AND
METHOD FOR THE PRODUCTION THEREOF

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Technical Field

~~The invention~~ This application relates to a multilayer ceramic component and a
method for producing the component. The component includes ~~comprising~~ a stack of
alternating ceramic layers and copper-containing electrode layers, which serve as internal
10 electrodes, ~~wherein~~ The internal electrodes are connected to external contacts that are
arranged on opposite, exterior sides of the stack, perpendicular to the multilayer structure,
~~and wherein~~ the Internal electrodes that are connected to different external contacts are in
interlocking engagement with one another.

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Background

A component of ~~this~~ foregoing type and a method for its production are known, for
example, from ~~the publication~~ DE 20023051.4. ~~The invention further relates to a method~~
~~for producing the above-named multilayer component.~~

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~~From the publication~~ DE 9700463 describes a method for producing green films
for multilayer piezoceramic components with Ag/Pd internal electrodes ~~is known~~, in
which a PZT-type piezoceramic powder (PZT = lead zirconate titanate) is used.

The material and/or the process used to fire on the external electrodes that ~~are contacted to~~ contact the internal electrodes should, in principle, be selected such that the electrode metal will not oxidize and the ceramic will not be reduced. For this reason, a precious metal or a precious metal alloy is customarily used as the electrode material.

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~~In the publication~~ DE 19945933, ~~for example, a~~ describes an exemplary method for producing external electrodes in piezoceramic components comprised of PZT ceramic and Ag/Pd internal electrodes ~~is described. The~~ In this method, contacting of the Ag/Pd internal electrodes is accomplished using a metal paste that has a silver content of > 65 % and an organic binder, which is fired on at approximately 700° C. The firing on of the metal paste is conducted in an air atmosphere, because aromatic compounds contained in the organic paste binder cannot be completely degraded under reductive conditions. However, this method is not suited to a multilayer component with PZT ceramic and copper-containing internal electrodes, since at customary debinding and/or firing-on temperatures, reduction of the PZT ceramic and oxidation of the metallic copper are prevented under only one specific, very low oxygen partial pressure of < 10⁻² Pa. Thus, the Ag/Pd external electrodes cannot be used in a multilayer ceramic component with copper-containing internal electrodes.

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~~With a component known from the publication~~ DE 20023051 U1 describes a component that is less costly than it is possible to avoid the high cost disadvantage of multilayer piezoceramic components that are based on a PZT ceramic and Ag/Pd internal

electrodes. This component uses ~~by using~~ copper-containing internal electrodes in place of the expensive Ag/Pd internal electrodes. However, DE 20023051 U1 ~~this publication~~ does not indicate which material would be suitable for firing on external electrodes in a piezoceramic component with copper-containing internal electrodes.

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Summary

~~The object of the invention is to disclose~~ Described herein is a multilayer ceramic component with internal electrodes and external contacts for contacting the internal electrodes, in which the bonding strength of the external contacts is sufficient. Also
10 described is ~~[[, and]]~~ a method for producing said the component, in which the ceramic is not reduced and in which neither internal nor external electrodes will oxidize.

~~The object of the invention is attained with a component of the type described at the beginning having the characterizing feature disclosed in claim 1, and with the process~~
15 ~~according to claim 11.~~

~~The invention discloses a multilayer~~ ceramic component of this application
contains ~~comprising~~ a stack of alternating ceramic layers and copper-containing electrode layers that serve as internal electrodes, ~~wherein~~ The internal electrodes are connected to
20 external contacts. The external contacts are arranged on exterior surfaces of the stack, opposite one another and perpendicular to the multilayer structure. ~~wherein~~ The internal electrodes that are connected to different external contacts are in interlocking engagement

with one another. The ~~multilayer component is characterized in that the~~ external contacts contain metallic copper, ~~wherein~~ The bonding strength of the external contacts to the stack ~~amounts to~~ is at least 50 N.

5 The ceramic layers ~~are preferably~~ may be comprised of ceramic green films that contain a thermohydrolytically degradable binding agent and can comprise a ferroelectric perovskite ceramic of the general composition ABO_3 , ~~especially such as~~ one of the PZT type $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$.

10 The ~~invention further discloses~~ application further describes a method for producing a ceramic component ~~as specified in the invention~~, in which the binder removal, or debinding, is performed and/or completed at a temperature of $\leq 300^\circ \text{C}$. The debinding takes place under a nitrogen stream with the addition of water vapor, ~~wherein~~ The water vapor partial pressure is set such that the corresponding oxygen partial
15 pressure at the given temperature ~~lies~~ is between the equilibrium points for $\text{Cu}/\text{Cu}_2\text{O}$ and PbTiO_3/Pb . The equilibrium point corresponds to an oxygen partial pressure at which both a reduced metal and a metal compound that corresponds to this metal are thermodynamically stable and can coexist without diffusing into one another.

20 ~~According to the invention~~, the Paste binders are completely separated out in a reduced atmosphere of, for example, $< 10^{-2} \text{ Pa}$ at a comparatively low temperature of $\leq 300^\circ \text{C}$, because at higher debinding temperatures, the oxygen, which is insufficient to

burn off the carbon contained in the organic binder, is partially drawn out of the ceramic lattice structure, which impairs the properties of the ceramic layers.

[[A]] Complete separation of organic constituents ~~is enabled according to the~~
invention in that the occurs because debinding is performed in a nitrogen stream that is
charged with water vapor, resulting in hydrolytic separation. The addition of the water
vapor causes the oxygen partial pressure to decrease thermodynamically. [[,]] However,
the oxygen partial pressure does not drop below a specific level at which the ceramic
would begin to reductively degrade.

On the other hand, the oxygen partial pressure also will not exceed a ~~certain~~ level
at which the metallic copper would begin to oxidize at the given temperature. Thus the
oxygen partial pressure is selected to be low enough so that the reduction processes in the
ceramic ~~remain~~ is adequately inhibited, while at the same time the copper contained in the
metal paste will not oxidize.

The oxygen partial pressure is maintained, or correspondingly adjusted, at all times
to correspond to the temperature. This occurs [[,]] not only during the debinding
process, but also during firing on of the metal paste, such that in the a p(T) diagram it lies
between the equilibrium points for Cu/Cu₂O and Pb/PbO at each process temperature.

The proportion of copper in the metal paste ~~is preferably~~ may be > 70%. Acrylic resin binders ~~are preferably~~ may be used as the organic paste binders.

The ~~invention~~ foregoing makes it possible to use a (copper-containing) metal paste
5 with an organic paste binder to produce external contacts in a piezoceramic component with internal electrodes that contain copper.

To produce the external contacts, a copper-containing metal paste having a copper content of > 70 m%, for example 78 m%, a glass flow, and an organic binder, for example
10 acrylic resin binder, ~~are preferably~~ may be used.

~~The~~ Glass flow (glass frit) ~~is preferably~~ may be comprised essentially of PbO and SiO₂, but may also contain other components, ~~for example~~ such as Na₂O, Al₂O₃ and BaO. The proportion of ~~the~~ glass flow in the metal paste ~~is preferably~~ may be less than 5 m%.
15 The composition and the proportion of the glass flow are selected such that the glass frit contained in the metal paste of the external contacts partially diffuses into the ceramic, thereby increasing the bonding strength of the external contacts to the sides of the stack.

First, using a known process[[,]] produces a stack ~~consisting~~ comprised of layers
20 of ceramic material and electrode layers placed one on top of another, which in a finished component correspond to the internal electrodes, ~~and layers of a ceramic material is~~
~~produced~~. The electrode layers are comprised of a copper-containing metal paste and can

be applied to the layers made of a ceramic material, for example, ~~by means of~~ via screen printing.

5 The copper-containing metal paste is also applied, for example, via screen printing, on opposite sides of the stack of internal electrodes and ceramic layers, which are positioned one on top of another.

10 The binder is removed from the metal paste in a moist nitrogen atmosphere in a gas-tight furnace at a temperature of $\leq 300^{\circ}\text{C}$, after which it is sintered at a higher temperature.

The copper-containing metal paste ~~is preferably~~ may be fired on at between 700 and 860°C .

15 To prevent the reduction of the lead oxide contained in the ceramic, lattice bases made of metallic copper, which serve simultaneously as gettering material, can be used in ~~the production of a component~~ described herein ~~as specified in the invention.~~

20 Below, the ~~invention~~ component, and method for its production, are will be described in greater detail with reference to exemplary embodiments and the associated drawings. The figures contain schematic, not-to-scale representations of various

exemplary embodiments ~~of the invention~~. Identical or equivalent components are assigned the same reference figures. ~~The drawings show~~

Description of the Drawings

5 Figure 1 ~~is~~ a perspective view of the structural design of a ceramic multilayer component, ~~of the invention~~

 Figure 2 ~~is~~ a half-logarithmic representation of oxygen partial pressure, which can be adjusted via the addition of water vapor, as a function of the temperature and the equilibrium curves for Cu/Cu₂O and Pb/PbTiO₃.

Detailed Description

10 ~~In~~ Figure 1 shows a ceramic component with copper-containing external contacts AK1 and AK2 ~~as specified in the invention is schematically illustrated~~. First copper-containing internal electrodes IE1 are connected to the first external contact AK1. Second
15 copper-containing internal electrodes IE2 are connected to the second external contact AK2. The internal electrodes are separated from one another by ceramic layers KS.

 The ceramic layers KS ~~preferably~~ may possess piezoelectric properties and ~~are~~
20 may be produced, for example, using the PZT-type ceramic.

The component ~~shown here specifically represents~~ of Figure 1 is a piezoelectric actuator. The electrode layers and ceramic layers stacked one on top of another are referred to herein as a piezo stack.

5 The fired-on external contacts AK1, AK2 ~~are preferably~~ may be between 10 and 20 μm , ~~for example thick, e.g., 15 μm , thick.~~ However, a different thickness for the external contacts may also be used ~~chosen~~.

10 The external contacts and/or internal electrodes ~~preferably~~ may contain a certain proportion of ceramic, which ~~preferably is~~ may be less than 50 m% (m% - percentage by mass), and which in one embodiment ~~preferred variant of the invention~~ is between 10 and 50 m%, e.g., ~~and which especially amounts to 40 m%.~~ In this embodiment, the ceramic proportion comprises ceramic particles having a specific grain size, for example, an average grain size of between 0.2 and 0.6 μm .

15 The ceramic portion in the metal paste serves ~~especially~~ to inhibit the formation of cracks and ~~the~~ separation of the external contact from the piezo stack, which can result from ~~the~~ different expansion properties of the ceramic material and ~~the~~ metallic copper.

20 The thermal expansion coefficient of ~~the~~ PZT-type ceramic within the temperature range extending from room temperature to the Curie temperature is approximately 1.5 - 2.0 ppm/K. In, ~~while within~~ the same temperature range, metallic copper ~~demonstrates~~

has a substantially higher thermal expansion coefficient of approximately 19 ppm/K. By admixing the ceramic material into the metal paste, the expansion characteristics of the external contact are adjusted to the expansion behavior of the ceramic stack both for the processing of the component and for its later applications within the specified temperature range of, for example, -50° C to +150° C, wherein, for example, the application of an electrical field causes a deformation of the component.

To adjust the thermal expansion coefficient, a glass frit that contains a high proportion of SiO₂, for example 39 m%, ~~is preferably~~ may be used, since SiO₂ has a high affinity for PZT-type ceramic.

In ~~the~~ preparation of the copper-containing metal paste, first a ceramic powder having an average grain size of, for example, 0.4 µm is dispersed in a solvent. The ceramic powder dispersion is then stirred into the copper-containing metal paste of the above-named composition, and is homogenized using a three-roller drawing machine. The viscosity of the metal paste ~~preferably amounts to~~ may be between 10 and 20 Pas. Once the finished metal paste has been applied to the side surfaces of the piezo stack, the paste is dried at approximately 80 to 140° C in an air atmosphere. This is followed by [[a]] debinding and sintering under the foregoing specified conditions ~~specified in the invention~~, in which ~~the~~ oxidation of ~~the~~ metallic copper and ~~the~~ reduction of ~~the~~ PbO or PbTiO₃ are prevented. In this embodiment, ~~especially in the~~ selection of the debinding temperature and the duration of the debinding process, ~~the focus is on ensuring~~ ensures

that, during the debinding process, both the binder components and the residual solvent will be completely burned out of the metal paste.

Because the glass frit contained in the metal paste can diffuse quite extensively
5 into the ceramic, leaving behind hollow cavities in the sintered ceramic layers, the sinter temperature is selected to be low enough (for example, 765° C) that the glass additive can penetrate only in the area of the internal electrodes. Microscopic studies have shown that at such a sinter temperature glass portions, above all silicon oxide, can be detected ~~only~~
10 within a narrow area of the ceramic layers that is adjacent to the external contacts. The external contacts adhere firmly and can be detached from the piezo stack ~~only~~ with the application of a high level of force, greater than 50 N. With the forceful detachment of the external contacts, portions of the ceramic material are broken off, which indicates a high level of bonding strength for the external contacts on the piezo stack.

15 The ceramic proportion ~~preferably amounts to~~ may be 40 m% relative to the solids content of the metal paste. ~~In principle~~ This metal paste can also be used for internal electrode layers.

~~It is also within the scope of the invention to use a preferably~~ A chemically active
20 ceramic powder (or even some other chemically active additive), hereinafter also referred to as a ceramic additive, may be present in the electrode metallization, which under certain circumstances can react chemically with the electrode metal, the organic binder,

the ceramic, and/or a reaction product of the latter, or can chemically bind certain components. Furthermore, the ceramic additive can react with the process atmosphere, for example, it can release the oxygen into the process atmosphere or ~~conversely~~ can absorb oxygen so that it, ~~whereby~~ the oxygen partial pressure is stabilized at least locally or temporarily. With a stable oxygen partial pressure, it is possible especially to protect the internal electrode layers or the external contacts from oxidation and to protect the ceramic layers from reduction. The ceramic powder additive ensures that a metal oxide that has been formed as a result of process instabilities in the electrode metallization is bonded, thus preventing an undesirable diffusion of this metal oxide into the ceramic layers.

The process of using a chemically inert ceramic powder in a metal paste, for example, to retard the sintering of the metal, is known in the art. ~~According to the invention~~ In this application, however, the ceramic powder is used as a functional additive that is chemically active and can chemically react with its environment. The chemical activity can be focused, for example, on the binding of Pb, which is released from the lead-containing ceramic material during sintering. It is also possible for the chemically active ceramic powder to bind another component from the ceramic mass especially during sintering, or to promote the release of certain components, such as, ~~for example~~, oxygen from the ceramic mass or from the binder contained in the ceramic mass or in the metal paste. ~~It is a requirement, however, that~~ The ceramic powder ~~will~~ should not chemically react with the metal portion of the metal paste.

In contrast to the metal paste that is used for the external electrodes, in the metal paste that is suitable for use in the internal electrode layers, preferably no glass additives are used. $(\text{Zr},\text{Ti})\text{O}_2$ is particularly well suited for use as the chemically active ceramic powder. In place of a chemically active ceramic powder, the metal paste can also contain
5 another chemically active additive, or in addition to the chemically active ceramic powder it may contain portions of other substances, for example BaO_2 and/or MgO .

The addition of a ceramic powder in the case of the internal electrodes further serves to improve adhesion between the internal electrodes and the ceramic layers that
10 surround them. ~~wherein~~ A fine distribution of the ceramic particles among the metal particles especially serves to prevent sinter neck formation. The sinter necks represent a localized disconnection of the internal electrodes, in which the metal coating becomes detached from the ceramic layer and/or becomes pulled back - especially around the edges - so that the internal electrodes assume a net-like structure, which is not replicable from
15 component to component. The method of achieving a homogeneous internal electrode structure by adding a precious metal or a precious metal alloy is known in the art. However, the addition of the ceramic powder as described herein ~~as specified in the invention~~ also provides a substantial cost advantage ~~relative to this~~ over the known method.

20 Figure 2 shows a half-logarithmic representation of an oxygen partial pressure p_{O_2} that can be adjusted based upon the temperature - ~~according to the invention~~ by adding

water vapor - and is illustrated by way of example by the curve 3, the numerically calculated equilibrium curve 1 for Cu and Cu₂O, and the numerically calculated equilibrium curve 2 for Pb and PbTiO₃.

5 The equilibrium curve 1 indicates the partial pressure of O₂ at the selected temperature, at which metallic Cu and Cu₂O can coexist. Metallic copper exists only at an oxygen partial pressure p_{O_2} that does not exceed the equilibrium level, i.e. below the equilibrium curve 1. Because only Cu₂O is stable above the curve 1, at an oxygen partial pressure that exceeds the equilibrium value at the selected temperature an undesirable
10 oxidation of the metallic copper will occur.

 The equilibrium curve 2 indicates the partial pressure for O₂ at the selected temperature, at which metallic Pb and PbTiO₃ can coexist. PbTiO₃ exists only above the curve 2. At an oxygen partial pressure p_{O_2} that drops below the equilibrium level at the
15 selected temperature, the PbTiO₃ contained in the ceramic will be reduced to Pb.

 For this reason, at least during the debinding phase of a process ~~of the invention~~ for producing ~~[[a]]~~ the above-described multilayer ceramic component, the oxygen partial pressure p_{O_2} is adjusted by adding water vapor such that ~~it~~ the oxygen partial pressure does
20 not exceed the maximum level p_{max} as defined by the curve 1, at which metallic copper is still stable, but also will not drop below the minimum level p_{min} as indicated by the curve 2, at which lead titanate is not yet reduced, i.e., $p_{min} < p_{O_2} < p_{max}$ at the given debinding

temperature T_E . The permissible range for adjustment of the oxygen partial pressure ~~thus~~
lies is between the curves 1 and 2.

5 ~~The Curve 3 describes~~ shows an optimal oxygen partial pressure ~~as defined by the~~
~~invention~~, to be established based upon temperature and within a moist atmosphere. The
quantity of water vapor to be added can be calculated in principle from the curve 3. It is
also possible to manually or automatically control the drop in the oxygen partial pressure
by adding water vapor, in such a way that the preset threshold values are not exceeded.

List of Reference Figures

- 1 ——— Characteristic curve for the equilibrium of Cu and Cu_2O in the diagram
 $\log\{p(\text{O}_2)\}$ plotted against temperature
- 5 2 ——— Characteristic curve for the equilibrium of Pb and PbTiO_3 in the diagram
 $\log\{p(\text{O}_2)\}$ plotted against temperature
- 3 ——— Characteristic curve for oxygen partial pressure, adjusted via the addition
of water vapor, as a function of temperature
- AK1, AK2 — External contact
- 10 KS — Ceramic layer
- IE1 — Internal electrodes connected to the external contact AK1
- IE2 — Internal electrodes connected to the external contact AK2
- p_{O_2} — Oxygen partial pressure
- p_{min} — Minimum permissible oxygen partial pressure
- 15 p_{max} — Maximum permissible oxygen partial pressure
- T_{E} — Debinding temperature

~~Patent Claims~~ What is claimed is:

1. Multilayer ceramic component with a stack of alternating ceramic layers (KS) and electrode layers that serve as internal electrodes, wherein the internal electrodes (IE1, IE2) are connected to external contacts (AK1, AK2), which are arranged on opposite external sides of the stack, perpendicular to the multilayer structure, wherein the internal electrodes that are connected to different external contacts are in interlocking engagement with one another, wherein the electrode layers contain copper,

characterized in that

the external contacts (AK1, AK2) contain metallic copper, wherein in the boundary area that lies adjacent to the boundary surface between the external contacts and the ceramic layers the external contacts are not oxidized and the material of the ceramic layers is not reduced,

wherein the bonding strength of the external contacts on the stack exceeds 50 N.

2. Component according to claim 1, in which the external contacts (AK1, AK2) contain a proportion of ceramic.

3. Component according to claim 1 or 2, in which the internal electrodes contain a proportion of ceramic.

4. Component according to claim 2 or 3, in which the ceramic proportion is ≤ 50 m%.

5. Component according to claim 4, in which the ceramic proportion lies between 10 and 50 m%.

6. Component according to one of claims 2 through 5, in which the ceramic proportion contains ceramic particles having an average grain size of between 0.2 and 0.6 μm .

7. Component according to one of claims 1 through 6, which is produced from ceramic green films that contain a thermohydrolytically degradable binding agent.

8. Component according to one of claims 1 through 7, in which the ceramic layers comprise a ferroelectric perovskite ceramic of the general composition ABO_3 .

9. Component according to claim 8, in which the perovskite ceramic is of the PZT type $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ wherein $1 \geq x \geq 0$.

10. Component according to one of claims 1 through 9, in which the thickness of the external contacts lies between 10 and 20 μm .

11. Method for producing a component according to one of claims 1 through 10,
in which the debinding is conducted at a temperature of $\leq 300^{\circ}\text{C}$ in a nitrogen stream
with the addition of water vapor, and in this manner the debinding process is completed,
5 wherein, at least during the debinding process, the oxygen partial pressure does
not drop below a level of p_{\min} , at which the ceramic will begin to reductively degrade,
 wherein the oxygen partial pressure does not exceed a level of p_{\max} , at which the
metallic copper will begin to oxidize at the given temperature.

10 12. Method according to claim 11,
 wherein p_{\min} corresponds to the equilibrium point for $\text{Cu}/\text{Cu}_2\text{O}$,
 wherein p_{\max} corresponds to the equilibrium point for Pb/PbO or Pb/PbTiO_3 .

13. Method according to claim 11 or 12, in which to produce external contacts a
15 copper-containing metal paste comprising a copper content of $> 70\text{ m\%}$, a glass frit and an
organic binder is used.

14. Method according to claim 13, in which an acrylic resin binder is used as the
organic binder.

20 15. Method according to claim 13 or 14, in which the glass flow contains
essentially PbO and SiO_2 .

16. Method according to one of claims 13 through 15, in which the copper-containing metal paste is fired on at between 700 and 860° C.

5 17. Method according to claim 16, in which the debinding and the firing on of the copper-containing metal paste are performed on a copper base layer.

18. Method according to one of claims 13 through 17, in which the copper-containing metal paste is applied by means of a screen printing process.

10 19. Method for producing a multilayer ceramic component with alternating ceramic layers and internal electrode layers,
in which a ceramic mass is used to create the ceramic layers,
in which a metal paste that contains a portion of a chemically active additive is
15 used to create the internal electrode layers,
wherein the chemically active additive reacts chemically with at least one component in its environment other than the metal portion of the metal paste.

20 20. Method according to claim 19, in which a chemically active ceramic powder is used as the chemically active additive.

21. Method according to claim 19 or 20, in which the components of the environment are selected from oxygen, at least one component of the ceramic mass and a binder or solvent that is contained in the metal paste or the ceramic mass.

5 22. Method according to one of claims 19 through 21, in which lead-containing ceramic mass is used,

 wherein as a result of a chemical reaction between the chemically active additive and its environment, oxygen is released and/or Pb and/or Cu are bonded.

10 23. Method according to one of claims 19 through 22, in which at least one additive is used as the chemically active additive, selected from the group of (Zr, Ti)O₂, MgO and BaO₂.

 24. Method according to one of claims 19 through 23, in which a non-precious
15 metal is used as the metal portion of the metal paste.

 25. Method according to claim 24, in which Cu or Ni is used as the metal portion of the metal paste.

Abstract

The invention relates to a multilayer ceramic component comprising a stack of alternating ceramic layers and copper-containing electrode layers that serve as internal electrodes, which are connected to external contacts, and to methods for producing said component. According to the invention the external contacts contain metallic copper, wherein in the boundary region that lies adjacent to the boundary surface between the external contacts and the ceramic layers, the external contacts are not oxidized and the material of the ceramic layers is not reduced, and wherein the bonding strength of the external contacts on the stack exceeds a level of 50 N. According to the invention, the debinding is conducted at a comparatively low temperature of max 300° C in a moist nitrogen atmosphere.

~~Figure 1~~